PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51)	International Patent Classification	5	:	_
	G02F 1/153, 1/155			

A1

(11) Internati nal Publication Number:

WO 94/15247

| '

(43) International Publication Date:

7 July 1994 (07.07.94)

(21) International Application Number:

PCT/US93/12529

(22) International Filing Date:

22 December 1993 (22.12.93)

(30) Priority Data:

07/996,676

24 December 1992 (24.12.92) US

(71) Applicant: SUN ACTIVE GLASS ELECTROCHROMICS, INC. [US/US]; 704 Executive Boulevard, Valley Cottage, NY 10989 (US).

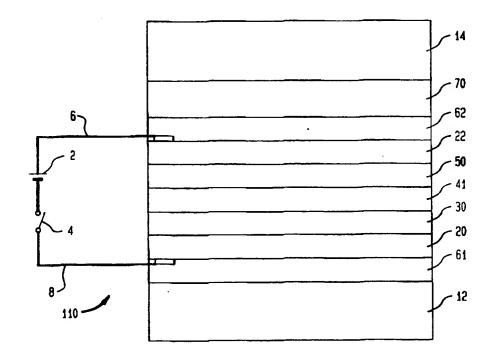
(72) Inventors: ELLIS, Frank, B., Jr.; 42 Mountadale Circle, Princeton, NJ 08540 (US). VAN DINE, John, E.; 26 Bartholf Lane, Mahwah, NJ 07430 (US). PARKHE, V., D.; 1120 Blueberry Court, Edison, NJ 08817 (US).

(74) Agents: LITTENBERG, Joseph, S. et al.; Lerner, David, Littenberg, Krumholz & Mentlik, 600 South Avenue West, Westfield, NJ 07090 (US). (81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CZ, DE, DK, ES, FI, GB, HU, JP, KP, KR, KZ, LK, LU, LV, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SK, UA, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published

With international search report.

(54) Title: ELECTROCHROMIC DEVICES



(57) Abstract

Electrochromic devices (100, 110, 120, 130, 140, 150) are disclosed which may be used for large surface area applications. The devices utilize optical tuning layers (60, 61, 62, 63, 64, 65) to minimize optical interference between layers of the structure and to maximize uniform optical transparency. Optical tuning also enables transparent conductive oxide layers (20, 22) to be replaced by thin conductive metal layers (21, 23), thereby reducing the overall thickness of these devices and facilitating the manufacturing process.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
ΑU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	Œ	Ireland	NZ	New Zealand
BJ	Benin	IT	İtaly	PL	Poland
BR	Brazil	JР	Japan	PT	Portugal
BY	Belarus	KE	Кепуа	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic	SD	Sudan
CG	Congo		of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
cs	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Мопасо	TT	Trinidad and Tobago
DK	Denmark	MOD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
Fī	Finland	MIL	Mali	UZ	Uzbekistan
FR	France	MIN	Mongolia	VN	Viet Nam
GA	Gabon		-		

20

25

30

35

-1-

DESCRIPTION

ELECTROCHROMIC DEVICES

The present application a continuation-in-part of application Serial No. 07/754,650, filed September 4, 1991.

Technical Field

The present invention relates to electrochromic devices through which energy, including light, can be transmitted under controlled conditions. More particularly, the present invention is directed to improved electrochromic devices which are usable over large surfaces, as well as methods for manufacturing these devices.

15 Background Art

materials, referred to as Certain electrochromic materials, are known to change their optical properties in response to the application of an electric current or an electric potential. been taken advantage of to property has electrochromic devices which can be controlled to selectively. transmit energy optical typically have structure electrochromic devices a consisting of sequential layers including a layer of an electrically conducting material, an electrode formed from a layer of an electrochromic material, an ion conductive layer, a counterelectrode layer, and another electrically conductive layer. In a first condition of the electrochromic device, each of the aforementioned layers is optically transparent such that a majority of optical energy incident on the device will Upon the application of an transmitted therethrough. electric potential across these layers, however, the optical properties of the electrochromic material will change such that the electrochromic layer will become less transparent, thereby preventing the transmission of much of the optical energy.

-2-

One of the most significant potential uses of electrochromic devices is to control transmission of optical energy through windows, and particularly the large windows of office buildings and other such structures. By selectively controlling the transmission of optical energy through these windows, tremendous cost savings in terms of heating and cooling these buildings can be realized. To date, however, efforts to capitalize on this potential benefit have largely failed. One reason for this failure has been the inability of the industry to produce economically an electrochromic device that can be used effectively over large surfaces. Those devices which have been available heretofore have exhibited an undesirable mosaic of different colors or an iridescent affect when used over large surface areas. Since the color of these devices is directly related to the thicknesses of the various layers, variations in layer thickness result in color changes from region to region, thereby producing this iridescent affect. The extremely tight tolerances which are required to overcome this difficulty make the use of devices for large surface area applications largely uneconomical.

further obstacle to the widespread commercialization of large surface area electrochromic devices relates to the understanding in this field that optically transparent conductive materials must be used to apply an electric potential across these devices so that the optical transparency of these devices will not be compromised. Preferably, the conductive formed from these materials have a low sheet resistance in order to effect a sufficiently rapid and uniform change in optical properties throughout the device. These layers are typically formed from transparent conductive metal oxides. The relatively thick layers of these oxides needed to get an acceptably low sheet resistance for large surface area devices tends to decrease their overall transparency. Moreover,

5

10

15

20

25

30

10

15

20

25

30

35

in view of the high cost of these materials, the relatively large quantities required makes the use of these materials uneconomical.

There therefore exists a need for improved electrochromic devices which will provide an acceptable appearance when used over large surface areas. There exists a further need for such electrochromic devices which can be produced efficiently and economically, and which therefore will be available for widespread commercial use.

Summary of the Invention

The present invention addresses these needs.

One aspect of the present invention provides an electrochromic device consisting of an electrochromic electrode including an formed from an structure electrochromic material, а counterelectrode @and transporting means for transporting ions between the electrode and the counterelectrode. Conductive means including at least two electrically conductive layers electrochromic structure sandwich the so that. electric potential can be applied to the structure. The electrochromic device further includes enhancing means for enhancing the transmission of radiation through at one of the electrically conductive Preferably, the electrode, the counterelectrode and the ion conductive layers are selected to all have about the same index of refraction.

In preferred embodiments, the enhancing means comprises at least one layer of an optically transparent material in surface contact with the at least one electrically conductive layer. Preferably, the optically transparent material is a transparent oxide, a transparent nitride, or a combination thereof. In some highly preferred embodiments, the optically transparent material comprises a mixture of silicon oxide and tin oxide.

The transporting means desirably includes at least one layer formed from an ion conducting material

-4-

sandwiched between the electrode and the counterelectrode. In these embodiments. the electrochromic material is preferably formed tungsten oxide, niobium oxide, titanium oxide, molybdenum oxide, oxide, nickel iridium oxide, mixtures thereof. The counterelectrode is preferably formed from vanadium oxide, niobium oxide, indium oxide, nickel oxide, cobalt oxide, molybdenum oxide or mixtures The ion conducting material may be a lithium thereof. conducting material such as lithium lithium borosilicate, lithium aluminum silicate, lithium niobate, lithium nitride, or lithium aluminum fluoride. Alternatively, the ion conducting material may be a hydrogen ion conducting material such as silicon dioxide or tantalum pentoxide. Preferably, the electrode, the counterelectrode and the ion conducting selected to all have about the same index of refraction. This may be accomplished by adjusting the index of refraction of these materials by additions of oxides having different indices of refraction.

In one embodiment in accordance with this aspect of invention, the the electrochromic device further includes a base material in surface contact with the at least one layer of an optically transparent material, the base material having a first index of 25 refraction, the at least one electrically conductive layer having a second index of refraction, and the at least one layer of an optically transparent material having a third index of refraction between the first and 30 second indices of refraction. In preferred electrochromic devices in accordance with embodiment, the index of refraction of the at least one layer of an optically transparent material is about equal to the square root of the mathematical product of the first and second indices of refraction. 35 at least one layer of an optically transparent material preferably has a thickness which is proportional to the index of refraction of the at least

5

10

15

10

15

20

25

30

35

one layer of an optically transparent material, and more preferably between about 60 nm and about 90 nm.

In another embodiment, the enhancing means may consist of a series of optically transparent layers beginning with a first optically transparent layer in surface contact with the at least one electrically conductive layer and ending with an nth optically This embodiment of the device may transparent layer. further consist of a base material in surface contact with the nth optically transparent layer, the at least one electrically conductive layer having a first index of refraction and the base material having a second refraction less than the first index of index of refraction. In this embodiment, the index of refraction of the first optically transparent layer is less than the first index of refraction, the index of refraction of the nth optically transparent layer is greater than the second index of refraction, and the index of refraction of each one of the series of optically transparent layers decreases monotonically from the index of refraction of the first transparent layer to the index of refraction of the nth transparent layer.

In still another embodiment, the enhancing means may consist of two optically transparent layers, one of the optically transparent layers being in surface contact with the at least one electrically conductive layer and another of the optically transparent layers surface contact with the one optically in In this embodiment, the at least one transparent layer. electrically conductive layer has a first index of refraction, the one of the optically transparent layers has an index of refraction which is less than the first index of refraction, and the another of the optically transparent layers has an index of refraction which is greater than the index of refraction of the one of the In preferred embodiments optically transparent layers. of this device, the one of the optically transparent layers has an index of refraction between about 1.4 and

10

15

20

25

30

35

about 1.7, and the other of the optically transparent layers has an index of refraction about equal to or greater than the first index of refraction. Further, the two optically transparent layers of preferred devices in accordance with this embodiment have a combined thickness of between about 30 nm and about 70 nm.

In yet another embodiment, at least one of the electrically conductive layers includes a layer of a first electrically conductive metal. Preferably, this electrically conductive metal layer thickness of between about 5 nm and about 15 nm, more preferably between about 7 nm and about Optionally, this embodiment may further include intermediate layer disposed between the electrochromic structure and the first electrically conductive metal This intermediate layer may be formed from a second electrically conductive metal, and preferably a metal which is more stable than the first electrically conductive metal, or from an electrically conductive oxide.

Preferably, the enhancing means in this last embodiment includes at least one layer of an optically transparent material in surface contact with the first electrically conductive metallayer. Still preferably, the optically transparent material comprises an electrically conductive oxide. Preferred optically transparent materials have an index of refraction greater than about 1.9, and desirably between about 1.9 and about 2.8, and a thickness of between about 10 nm and about 50 nm, and more preferably between about 23 nm and about 45 nm.

In still another embodiment of the present invention, at least one of the electrically conductive layers includes a layer of an electrically conductive oxide, and preferably an oxide having about the same of refraction as the electrode, the counterelectrode and the ion conducting layer.

-7-

devices in accordance with Electrochromic this embodiment may further include a layer of electrically conductive metal in surface contact with the electrically conductive oxide layer. In preferred embodiments, the electrically conductive oxide layer is disposed between the electrochromic structure and the Desirably, the enhancing means conductive metal layer. in these embodiments includes at least one layer of an optically transparent material having index refraction greater than about 1.9 in surface contact with the conductive metal layer. Preferably, these optically transparent layers have a thickness of between about 10 nm and about 50 nm.

further aspect of the present invention provides an electrochromic combination consisting of a substrate and an electrochromic transparent the transparent substrate. The arranged on electrochromic device may generally consist of electrochromic structure including an electrode formed from an electrochromic material, a counterelectrode and transporting means for transporting ions between the electrode and the counterelectrode. The electrochromic device may further consist of conductive means including at least two electrically conductive layers sandwiching the electrochromic structure for applying an electric potential to the electrochromic structure, and enhancing for enhancing the transmission of radiation through at least one of the electrically conductive layers.

Preferred embodiments in accordance with this aspect of the present invention may further include a transparent superstrate, wherein the electrochromic device is sandwiched between the transparent substrate and the transparent superstrate. A layer of an adhesive material may be used to bind the transparent superstrate to the electrochromic device. Such adhesive layer preferably has an index of refraction between about 1.4 and about 1.8, which index of refraction is preferably

5

10

15

20

25

30

-8-

substantially equal to the index of refraction of the superstrate. Optionally, the at least one electrically conductive layer may include a layer of an electrically conductive oxide, and the adhesive layer may be in surface contact with the electrically conductive oxide layer. In that event, the adhesive layer preferably has an index of refraction between the index of refraction of the electrically conductive oxide layer and the index of refraction of the superstrate.

10 <u>Brief Description of the Drawings</u>

5

15

25

30

A more complete appreciation of the subject matter of the present invention and the various advantages thereof can be realized by reference to the following detailed description, in which reference is made to the accompanying drawings in which:

FIGURE 1 is a highly schematic crosssectional view of an electrochromic device in accordance with the prior art;

FIGURE 2 is a graphical representation 20 showing the optical transmission of the electrochromic device of FIGURE 1 in the bleached state;

FIGURE 3 is a highly schematic crosssectional view of an electrochromic device in accordance with one embodiment of the present invention;

FIGURE 4 is a highly schematic crosssectional view of an electrochromic device in accordance with another embodiment of the present invention;

FIGURE 5 is a graphical representation showing the optical transmission of the electrochromic device of FIGURE 4 in the bleached state;

FIGURE 6 is a highly schematic crosssectional view of an electrochromic device in accordance with a further embodiment of the present invention;

FIGURE 7 is a graphical representation 35 showing the optical transmission of the electrochromic device of FIGURE 6 in the bleached state; WO 94/15247 PCT/US93/12529

-9-

FIGURE 8 is a highly schematic crosssectional view of an electrochromic device in accordance with still another embodiment of the present invention;

FIGURE 9 is a graphical representation showing the optical transmission of the electrochromic device of FIGURE 8 in the bleached state;

FIGURE 10 is a highly schematic crosssectional view of an electrochromic device in accordance with yet another embodiment of the present invention; and

FIGURE 11 is a highly schematic crosssectional view of an electrochromic device in accordance with a still further embodiment of the present invention.

44

15 Best Mode of Carrying Out the Invention

For the purpose of the present description, the electrochromic devices of the present invention are discussed in connection with their use to control the transmission of light through a window. It will be appreciated, however, that these electrochromic devices are useful in a wide variety of applications, including display devices, variable reflectance mirrors, lenses and similar devices in which the ability to selectively control the transmission of optical energy through a transparent structure would be beneficial.

A window 10 incorporating an electrochromic in accordance with the prior art is schematically in cross-section in Figure 1. consists of a series of sequential layers, including a transparent glass substrate 12, a transparent conductive oxide layer 20, an electrochromic electrode layer 30, an ion conducting layer 40, a counterelectrode layer 50, another transparent conductive oxide layer 22, transparent glass superstrate 14. A low voltage battery 2 and switch 4 are connected to the layered structure by means of conductive wires 6 and 8. In order to alter the optical properties of window 10, switch 4 is closed whereupon battery 2 will cause an electric potential to

5

10

20

25

30

be created across the layered structure. The polarity of the battery will govern the nature of the electric potential created and thus the direction of ion and electron flow. In the embodiment shown in Figure 1, the electric potential created as switch 4 is closed will cause ions to flow from the counterelectrode layer 50 through the ion conducting layer 40 to the electrochromic electrode layer 30, thereby reducing the so-called electrochromic material to its In this state, the transparency of window 10 is substantially reduced as a large portion of the optical energy incident on window 10 is absorbed and reflected by the electrochromic electrode layer 30. Window 10 is said to have a "memory" in that electrochromic layer 30 will remain in this colored state even when switch 4 is opened, provided laver 40 is also electrically insulating. However, when the polarity of battery 2 is reversed and switch 4 is closed, the applied electric potential will cause ions to flow in a reverse direction from the electrochromic electrode layer 30 through the ion conducting layer 40 to the counterelectrode layer 50, thereby oxidizing the electrochromic material to its so-called "bleached" state in which the transparency of window 10 is at a maximum.

fabricating window 10 described layers 20 and 22 may be formed from any transparent oxides which are highly electron conducting, such as doped tin oxide, doped zinc oxide, tin-doped indium oxide and similar materials. The materials for forming layers 20 and 22 need not be the same. Electrochromic electrode layer 30 is typically formed from a material whose optical properties can be reversibly altered as its state of oxidation changes. The thickness electrochromic electrode layer 30 will normally be such that, in the colored state, an acceptable reduction in the transparency of the window is obtained. A widely used material in this regard is tungsten oxide (WO3), although other suitable materials may be used, such as

5

10

15

20

25

30

WO 94/15247 PCT/US93/12529

-11-

molybdenum oxide, nickel oxide, iridium oxide, niobium oxide, titanium oxide and mixtures of the foregoing oxides. The ion conducting layer 40 is used to transport ions into and out from the electrochromic layer 30, and must exhibit and maintain two electrically opposed properties. That is, ion conducting layer 40 must readily transmit ions upon the application of an must electric potential, yet remain electrically with respect the insulating to transmission In that regard, ion conducting layer 40 electrons. thickness sufficient to have possibility of electron arcing or shorting between the electrochromic electrode layer 30 and the counterelectrode layer 50. Suitable materials for forming layer 40 for the transmission of lithium ions include, for example, lithium silicate, lithium borosilicate, lithium aluminum silicate, lithium niobate, lithium nitride and lithium aluminum fluoride; and suitable materials for transmitting hydrogen ions include tantalum pentoxide silicon and Alternatively, ion conducting layer 40 may be formed from a polymer material.

The counterelectrode layer 50 of window 10 is typically formed from a material which is capable of storing ions and then releasing these ions transmission to electrochromic layer 30 in response to an appropriate electric potential. The thickness of this layer is preferably such that the counterelectrode is capable of transmitting a large enough quantity of ions to the electrochromic electrode layer to effect in layer an acceptable change in color. Some counterelectrode materials are themselves electrochromic in that their optical properties also change as they give up or receive ions in response to application of an electric potential. the These electrochromic counterelectrode materials may complement the affect that an electric potential has on the optical properties of the electrochromic electrode materials.

5

10

15

20

25

30

-12-

That is, these counterelectrode materials may become less transparent as they release ions to convert the electrochromic materials to the colored state. Similarly, the counterelectrode materials may become transparent as they receive ions upon the electrochromic material conversion of the the bleached state. Suitable materials for forming counterelectrode layer 50 include vanadium oxide, niobium oxide, indium oxide, nickel oxide, cobalt oxide, molybdenum oxide and mixtures of the foregoing oxides.

Each of the layers described above may be deposited by known techniques, provided that discrete and continuous individual layers are formed. The particular method of deposition for each layer depends upon several parameters, including the material being deposited, the thickness of the layer being deposited, materials deposited in previous layers, Deposition techniques including RF sputtering, chemical deposition, plasma enhanced chemical vapor deposition, electron beam evaporation, sol-gel techniques and other known methods for depositing thin films are typically used.

During the fabrication process, at least one electrochromic electrode the layer 30 and counterelectrode layer 50 may be inserted with appropriate ions, such as lithium or hydrogen unless these ions are already present in one of these layers in its deposited form. Ion insertion may be accomplished by treating layer 30 or layer 50 with a suitable reducing agent. For example, n-butyl lithium may be used for lithium insertion, or aqueous sulfuric acid may be used for hydrogen insertion. Alternatively, ion insertion may be accomplished by a vacuum processing step, such as sputtering from a target serving as a source of suitable ions, such as a lithium target which decomposes to produce lithium atoms in the vapor phase. Also, hydrogen insertion may be accomplished by exposure to a hydrogen plasma. Ion insertion may also

5

10

15

20

25

30

WO 94/15247 PCT/US93/12529

-13-

electrochemically by accomplished reduction appropriate ion-containing electrolyte. A still further technique is to deposit a layer of the reduced material directly by vapor deposition in a reducing atmosphere which will react with the source or target material to form the desired composition, or by using a source or target having the reduced composition. Still another technique for insertion uses a volatile precursor and ignites a low vapor pressure discharge to dissociate the insertion ion from the precursor. For example, organic lithium compound in the form of a precursor may be dissociated so that lithium ions come into contact with the material into which they are to be inserted.

Figure 2 shows the transmission of optical energy as a function of wavelength in the bleached state for a window 10 in which glass substrate 12 has an index of refraction of 1.5, transparent conductive oxide layer 20 has an index of refraction of 2.1 and a thickness of 450 nm, electrochromic electrode layer 30 has an index of refraction of 2.1 and a thickness of 300 nm, conducting layer 40 has an index of refraction of 1.5 and a thickness of 200 nm, counterelectrode layer 50 has an index of refraction of 2.0 and a thickness of 200 nm, transparent conductive oxide layer 22 has an index of refraction of 2.1 and a thickness of 450 nm, and glass superstrate 14 has an index of refraction of 1.5. bleached stated is shown because it is more sensitive to difficulties the of achieving uniform transmission as a function of wavelength. As can be clearly seen, there is very little uniformity to the optical transmission through this layered structure, resulting in a window having a colored mosaic or iridescent affect.

One aspect of the present invention overcomes the economic disadvantage and reduces the optical difficulties associated with the use of transparent conductive oxides in large surface area optically

5

10

15

20

25

WO 94/15247 PCT/US93/12529

-14-

transparent electrochromic devices. An embodiment of a window 100 incorporating an electrochromic device in accordance with this aspect of the present invention is shown in schematic cross-section in Figure 3. 100 is similar to window 10 described above with the positions of the electrochromic electrode layer and the counterelectrode layer reversed. Thus, window includes transparent glass substrate 12, transparent conductive oxide layer 20, counterelectrode layer 50, ion conducting layer 40, and electrochromic electrode These layers are formed from substantially layer 30. the same materials as described above in connection with window 10. Rather than a second transparent conductive oxide layer 22, however, window 100 has a combination of including layers of a layer 21 formed electrically conductive metal and a layer 60 formed from a transparent oxide which serves as an optical tuning layer. Optionally, window 100 may also include a barrier 80 formed from layer inert an or stable electrically conductive metal, such as nickel, for preventing ions from migrating from electrochromic electrode layer 30 to conductive metal layer 21, and a second layer 90 which may promote adhesion of optical tuning layer 60 to conductive metal layer 21 or may act barrier to prevent the dissolution of conductive metal in layer 21 into transparent oxide The assembly is completed by a transparent layer 60. glass superstrate 14.

In the above-described structure, layer 21 may be formed from silver or another highly conductive 30 metal, such as copper or aluminum. By using a highly conductive metal, very thin layers having little optical absorption and low sheet resistance can be thereby overcoming the cost and manufacturing difficulties associated with the use of relatively thick 35 layers of transparent conductive oxides. Preferably, layer 21 has a thickness of between about 5 nm and about 15 nm, and more preferably between about 7 nm and about

5

10

15

20

10

15

20

25

30

35

Even though very thin layers of silver and other conductive metals are not highly optically transparent due to their high reflectivity, optical transmission therethrough may be improved by the presence of an appropriately selected optical tuning layer 60. Optical tuning layers, such as layer 60, which are used in combination with conductive metal layers preferably have a thickness between about 10 nm and about 50 nm, and more preferably between about 23 nm and about 40 nm. Preferred materials for forming optical tuning layer 60 have an index of refraction which is greater than about 1.9, and more preferably between about 1.9 and about When optical tuning layer 60 is formed with a thickness of about 30-40 nm and with an index of refraction which is substantially the same as or greater than that for counterelectrode 30 so that the conductive metal layer 21 having a low index of refraction is sandwiched between layers 60 and 30 having higher the reflected signals at the indices of refraction, various interfaces between layers 14, 60, 21, 30 and 40 reduced, thereby lowering reflection and As a result, window 100 will maximizing transmission. be largely optically transparent in the bleached state of the electrochromic electrode layer 30.

Further improvements in the transmission of optical energy through electrochromic devices can be realized by using the principle of an optical tuning above, in combination described layer, as transparent conductive oxide layers. Α window 110 incorporating such feature is shown in schematic cross-Window 110 consists of a glass section in Figure 4. substrate 12, a transparent optical tuning layer 61, a transparent conductive oxide layer 20, an electrochromic electrode layer 30, an ion conducting layer 41, counterelectrode layer 50, a transparent conductive oxide layer 22, a transparent optical tuning layer 62, a laminate layer 70, and a transparent glass superstrate Each of layers 12, 20, 30, 50 and 14 are the same

10

as described above in connection with window 100, with the positions of the electrochromic electrode layer 30 and the counterelectrode layer 50 reversed so that they are again in the orientation shown in Figure 1. In this embodiment, conductive metal layer 21 and optical tuning have been replaced with a transparent conductive oxide layer 22 which may or may not be formed from the same transparent conductive oxide as layer 20, appropriate optical tuning layer 62. addition, an optical tuning layer 61 has been inserted to improve upon the optical transmission through window and more particularly, to improve uniformity of the optical transmission as a function of wavelength.

The selection of appropriate optical tuning layers 61 and 62 is made with reference to the equation index of refraction = n + ik

where n is the real component of the index refraction, i is the square root of -1, and k is the imaginary component of the index of refraction related 20 to absorption. In order to optimize the optical tuning effect, layers 61 and 62 are selected so that they are transparent to visible light (i.e., the imaginary component of the index of refraction, k, 25 approximately equal to zero so there is absorption), and the real component of the index of refraction of these layers, n, is equal to the geometric mean of the indices of refraction of the layers on either side of these optical tuning layers. Thus, optical tuning layer 61 preferably is formed from a 30 transparent material having an index of refraction which equal to the geometric mean of the index refraction of glass substrate 12 and the index refraction of transparent conductive oxide layer 20. Similarly, optical tuning layer 62 preferably is formed 35 transparent material having an index refraction which is equal to the geometric mean of the indices of refraction of conductive oxide layer 22 and

10

15

20

25

30

35

laminate layer 70. As used herein, the "geometric mean" refers to the square root of the mathematical product of the two indices of refraction.

Proper optical tuning is also a function of the thickness of optical tuning layers 61 and 62 which to one-fourth the of optical is preferably equal The optical incident light. of the wavelength wavelength through a layer is determined by dividing the question by the index of light in wavelength of refraction of the medium through which it is passing, For visible light layers 61 and 62. 400-650 nm, a useful about wavelengths between optical wavelength can be made by approximation of index of dividing a wavelength of 540 nm by the refraction of the optical tuning layer. The thickness of the optical tuning layer can then be determined by dividing the optical wavelength by 4. Optical tuning layers used in combination with transparent conductive oxide layers, such as layers 20 and 22, desirably have a thickness of between about 60 nm and about 90 nm.

As an example of the foregoing, the following will demonstrate the method for selecting the index of refraction and thickness of optical tuning layer 61. Firstly, the desired index of refraction is determined by multiplying 1.5 (the index of refraction of glass substrate 12) times 2.1 (the index of refraction of transparent conductive oxide layer 20) and taking the square root of the product. This calculation yields an index of refraction of 1.77. The thickness of optical tuning layer 61 is then determined by dividing 540 nm by 1.77 to yield an optical wavelength of about 300 nm. Preferably, the thickness of optical tuning layer 61 is 75 nm. The this value, or about one-fourth of calculation for optical tuning layer 62 is performed in the same fashion.

Preferred materials for forming the discrete optical tuning layers of the present invention include transparent oxides, transparent nitrides, and a

-18-

combination transparent oxides of and transparent nitrides. Particularly preferred are mixtures of the oxides of silicon and tin. In these mixtures, silicon to tin ratio determines the index of refraction, with a higher silicon to tin ratio lowering the index of refraction and a lower silicon to tin ratio increasing the index of refraction. Other materials which can be used for the optical tuning layers are set forth in Gordon, U.S. Patent Nos. 4,187,336 and 4,308,316, the disclosures of which are hereby incorporated herein. appropriate selection of optical tuning layers 61 and 62 will minimize the optical interference at the interface between conductive oxide layer 20 and substrate 12 in the case of tuning layer 61, and at the interface between conductive oxide layer 22 and laminate layer 70 in the case of tuning layer 62.

Laminate layer 70 is an adhesive layer for adhering glass superstrate 14 to optical tuning layer 62. So that laminate layer 70 does not degrade the optical transmissivity of window 110, laminate layer 70 is preferably selected to have an index of refraction which is substantially the same as the index of refraction of glass superstrate 14, thereby minimizing any interference effects between these layers. In this regard, particularly suitable adhesives for laminate layer 70 are ethylene vinylacetate and polyvinylbutyral.

The electrochromic structure of window 110 is further distinguished from that of window 100 and prior art electrochromic devices in that the principle of optical tuning has been applied to ion conducting layer this case, optical interference the interfaces between ion conducting layer 41 the adjacent electrochromic electrode layer 30 and counterelectrode layer 50 can be substantially eliminated by forming ionic conducting layer 41 from a transparent material having an index of refraction which is approximately equal to the indices of refraction of electrochromic electrode layer 30 and counterelectrode

5

10

15

20

25

30

10

15

20

25

30

35

The indices of refraction of electrochromic layer 50. 30, ion conducting layer electrode layer counterelectrode layer 50 may be adjusted by mixing the materials for forming these layers with materials having higher or lower indices of refraction to obtain the For example, where it is desired to desired result. provide an ion conducting layer 41 having an index of greater than that provided by refraction silicate, mixtures of lithium silicate and titanium or zirconium may be used. When the indices of refraction of all three of these layers are approximately equal, interference at these interfaces will be substantially eliminated and optical transmission will be maximized.

In highly preferred embodiments, the indices of refraction of electrochromic electrode layer 30, ion conducting layer 41 and counterelectrode layer 50 are adjusted to be substantially similar to the indices of refraction of conductive oxide layers 20 and 22. Furthermore, because of the complementary nature of the above optical tuning processes, the thicknesses of layers 20 through 22 are no longer critical with respect to optical interference, thereby providing a much wider thickness tolerance during the formation of these layers.

Figure 5 shows the transmission of optical energy as a function of wavelength for a window 110 in the bleached state in which glass substrate 12 has an index of refraction of 1.5, optical tuning layer 61 has an index of refraction of 1.77 and a thickness of 75 nm, transparent conductive oxide layer 20 has an index of a thickness of 450 2.1 and nm, of refraction electrochromic electrode layer 30 has an of 2.1 and a thickness of 300 nm, ion refraction of conducting layer 41 has an index of refraction of 2.0 and a thickness of 200 nm, counterelectrode layer 50 has an index of refraction of 2.0 and a thickness of 200 nm, transparent conductive oxide layer 22 has an index of refraction of 2.1 and a thickness of 450 nm, optical tuning layer 62 has an index of refraction of 1.77 and a thickness of 75 nm, laminate layer 70 has an index of refraction of 1.5, and glass superstrate 14 has an index of refraction of 1.5. As clearly shown in Figure 5, the foregoing characteristics produce a window 110 which exhibits excellent uniformity with respect to optical transmission.

A window 120 in accordance with an alternate embodiment of the present invention is shown schematically in Figure 6. Window 120 is substantially the same as window 110 described above, except that optical tuning layer 61 has been replaced with a pair of optical tuning layers 63 and 64, and optical tuning layer 62 has been removed. The use of two optical tuning layers 63 and 64 provides advantages over the use of a single optical tuning layer. A first advantage is that two optical tuning layers provides an opportunity for more effective optical tuning to be achieved with a combined tuning layer thickness which is less than the thickness required for a single optical tuning layer. Another advantage to the use of two optical tuning layers is that each layer can be formed from more simple materials than can a single optical tuning thereby avoiding the complex chemistry required to form such single layers. Techniques using two layers for optical tuning are disclosed in Gordon, U.S. Patents Nos. 4,377,613 and 4,419,386, the disclosures of which are hereby incorporated herein.

Where two optical tuning layers 63 and 64 are used adjacent to one another, optical tuning may be achieved by selecting an optical tuning layer 64 which has an index of refraction which is significantly smaller than the index of refraction of layer 20, and by selecting an optical tuning layer 63 having an index of refraction which is significantly larger than the index of refraction of optical tuning layer 64, and most preferably which is substantially similar to the index of refraction of transparent conductive oxide layer 20.

5

10

15

20

25

30

10

15

20

25

30

the interference between In such combination, interfaces will substantially cancel and various various layers will be transmission through the maximized when layers 63 and 64 have appropriate Preferably, layer 64 will have an index of refraction between about 1.4 and 1.7 and layers 63 and 64 will have a combined thickness of between about 30 nm and about with layer 64 having a 70 nm. thickness than layer 63.

optical transmission shows the through window 120 in the bleached state as a function of wavelength, where glass substrate 12 has an index of refraction of 1.5, optical tuning layer 63 has an index of refraction of 2.1 and a thickness of 20 nm, optical tuning layer 64 has an index of refraction of 1.5 and a thickness of 29 nm, transparent conductive oxide bayer 20 has an index of refraction of 2.1 and a thickness of 450 nm, electrochromic electrode layer 30 has an index of refraction of 2.1 and a thickness of 300 nm, ion conducting layer 41 has an index of refraction of 2.0 and a thickness of 200 nm, counterelectrode layer 50 has an index of refraction of 2.0 and a thickness of 200 nm, transparent conductive oxide layer 22 has an index of refraction of 2.1 and a thickness of 450 nm, laminate layer 70 has an index of refraction of 1.5, and glass superstrate 14 has an index of refraction of 1.5. can be seen from this figure, the optical transmission through window 120 is more uniform than through windows formed with no optical tuning layers (such as window 10), but is less uniform than through window 110. primary reason for this inferior performance is the absence of an optical tuning layer between conductive oxide layer 22 and laminate layer 70 in the back end of the device.

An improvement in the optical transmission properties of window 120 can be achieved by adjusting the indices of refraction of electrochromic electrode layer 30, ion conducting layer 41 and counterelectrode

WO 94/15247 PCT/US93/12529

-22-

layer 50 so that they are more similar to one another and to the indices of refraction of transparent conductive oxide layers 20 and 22.

A further slight improvement in the optical transmission properties of window 120 can be achieved by optimizing the index of refraction of laminate layer 70. This can be achieved by using a laminate layer 70 having an index of refraction which is the geometric mean of the indices of refraction of the transparent conductive oxide layer 22 and the glass superstrate 14. Since laminate layer 70 serves to adhere superstrate 14 to transparent conductive oxide layer 22, there is little opportunity to vary the thickness of this layer.

Rather than the foregoing methods for 15 optically tuning transparent conductive oxide layer 20, this layer may be optically tuned by the use of two or more optical tuning layers selected so that the indices of refraction of the various layers gradually increase from the index of refraction of substrate 12 to the index of refraction of transparent conductive oxide 20 layer 20. In that regard, layers 63 and 64 of window may be replaced by two or more layers of monotonically increasing index of refraction. For example, for a device including a glass substrate 12 having an index of refraction of 1.5 and a transparent 25 conductive oxide layer 20 having an index of refraction of 1.9, optical tuning layer 63 will desirably have an index of refraction of about $(1.5^2 \times 1.9)^{-1/3}$ or 1.62. and optical tuning layer 64 will desirably have an index 30 of refraction of about $(1.5 \times 1.9^2)^{-1/3}$ or 1.76. thicknesses of layers 63 and 64 are desirably about 60 nm and 53 nm, respectively, as determined by optical modeling to achieve maximum transmission. desirable, a series of more than two adjacent optical tuning layers may be used to further enhance the optical 35 tuning affect.

For the embodiments of the invention having the structure of window 110 or window 120 described

5

10

15

20

25

30

35

it has been desirable that the transparent conductive oxide layers 20 and 22, the electrochromic electrode layer 30, the ion conducting layer 41, and the counterelectrode layer 50 all have about the same index When that is the case, the thicknesses of refraction. of these layers are largely immaterial and optimum optical tuning is achieved, i.e., these windows exhibit minimum amount of iridescence. If there substantial mismatch in the indices of refraction for these layers, however, some optical tuning may still be accomplished by adjusting the thicknesses of the layers. To illustrate, each of the layers of window 120 may have the indices of refraction and thicknesses as described above in connection with Figure 7, except that ion conducting layer 41 may have an index of refraction of To minimize iridescence in this scenario; the thickness of ion conducting layer 41 should be reduced to between about 130 nm and about 160 nm as determined by optical modeling to achieve maximum transmission through the window.

130 in accordance with a further embodiment of the present invention is shown in schematic cross-section in Figure 8. Window 130 is described above, with the similar to window 120 exception that transparent conductive oxide layer 22 has been replaced with a conductive metal layer 21 and an optical tuning layer 64. Layers 21 and 64 may be substantially similar to layers 21 and 60 of window 100 described above, and coact with the other layers in the same manner as in window 120 to provide an optically tuned, optically transparent electrochromic window.

Figure 9 shows the optical transmission as a function of wavelength in the bleached state of a window 130 whose layers have the same indices of refraction and thicknesses as described above in connection with window 120, and wherein conductive metal layer 21 is silver having a thickness of 10 nm and optical tuning layer 64 is a transparent oxide having an index of refraction of

-24-

2.5 and a thickness of 30 nm. As can be seen from this figure, the structure of window 130 provides good uniformity of optical transmission with respect to wavelength. Moreover, a comparison of Figures 7 and 9 indicates that windows that incorporate conductive metal layers can exhibit optical transmission which is similar to the optical transmission through windows which utilize transparent conductive oxide layers rather than conductive metal layers.

Still another embodiment of a window 140 10 accordance with the present invention schematically in Figure 10. Window 140 is substantially the same as window 130 described above, except that an intermediate layer 22 has been added between conductive 15 metal layer 21 and counterelectrode layer 50. embodiment, intermediate layer 22 is formed from a transparent electrically conductive oxide, combining with conductive metal layer 21 to provide a laminate having a lower overall sheet resistance which will improve switching time between the bleached and colored 20 states. This improved switching can thus accomplished without deteriorating the optical properties of the device as would happen if the thickness of the conductive metal layer 21 were 25 substantially increased. Further, transparent electrically conductive oxide layer 22 may serve as a diffusion barrier to prevent unwanted diffusion between the counterelectrode layer 50 and the conductive metal layer 21.

In another embodiment, intermediate layer 22 may be in the form of a metal layer having a thickness of less than about 2 nm. In this embodiment, the metal layer typically serves one of the same functions as layers formed from transparent electrically conductive oxides, that is it prevents unwanted diffusion between the counterelectrode layer 50 and the conductive metal layer 21. Preferred metals for forming layer 22 include metals which are highly stable or inert. A particularly

٠. .

15

· •

À

7

...

5

10

15

20

25

30

35

preferred metal in that regard is nickel. Regardless of the material for forming intermediate layer 22, optical tuning layer 64 again preferably has an index of refraction of greater than 1.9 and a thickness of between about 10 nm and about 50 nm.

A window 150 in accordance with yet another present invention is embodiment of the schematically in Figure 11. Window 150 is substantially the same as window 130, except that transparent oxide layer 20 and optical tuning layers 63 and 64 have been replaced by conductive metal layer 23 and optical tuning layer 65, respectively, thereby placing a constraint on the combined thickness of layers 30, 41 and 50. desirable in this embodiment that layers 30, 41 and 50 have similar indices of refraction and that the combined thickness of these layers be as thin as possible, subject to the restraint of a maximum transmission at a chosen wavelength between about 400 nm and 650 nm. example, if layers 30, 41 and 50 each have indices of refraction of about 2.2, then their combined thickness preferably would be about 50 nm or about 300 nm as by optical modeling to achieve determined optical transmission. In this embodiment, conductive metal layer 23 is similar to conductive metal layer 21, and optical tuning layer 65 is similar to optical tuning layer 64.

In another embodiment of the invention, (not shown) optical tuning layer 64 of window 130, 140 or 150 may be formed from an electrically conductive transparent oxide. In this event, the manufacture of these devices may be simplified by connecting wires 6 and 8 to layer 64 rather than to conductive metal layer 21, thereby avoiding the masking or etching steps which would otherwise be required.

As discussed above, the electrochromic devices of the present invention are typically built upon a substrate, such as glass substrate 12. This substrate not only supports the very thin layers of these devices

during fabrication and use, but also protects the layers from damage resulting from exposure to the environment. A superstrate, such as glass superstrate 14, provides further support and protection. Although each of the embodiments of the present invention have been described in connection with a substrate and a superstrate made from glass, other substrate and superstrate materials may be used, including transparent ceramic materials and rigid and flexible transparent plastics. In that regard, the embodiment shown in Figure 11 particularly applicable to plastic substrates since the conductive metal layer 23 can be applied at relatively low temperatures. Furthermore, it is contemplated that electrochromic devices may initially be formed plastic substrates and the entire assembly then applied to windows and other such structures.

Furthermore, the embodiments of the present invention discussed above contemplate the deposition of layers successively from substrate 12 to superstrate 14 usina ion conducting layers formed from ceramic materials. It will be appreciated, however, that optically tuned devices may be formed by assembling two "one-half" structures to opposite sides of a polymer sheet which will then serve as the ion conducting layer. For example, window 110 can be produced by forming layers 61, 20 and 30 on substrate 12, forming layers 62, 22 and 50 on superstrate 14 (layer 70 would no longer be necessary in this arrangement), and then sandwiching these two portions together around an ion conducting, electrically insulating polymer sheet which will thus serve as ion conducting layer 41.

Although the invention herein been described with reference to particular embodiments, is to be understood that these embodiments are merely illustrative of the principles and applications of the present invention. It is therefore to be understood numerous modifications may be made to illustrative embodiments and that other arrangements may

5

10

15

20

25

30

-27-

be devised without departing from the spirit and scope of the present invention as set forth in the appended claims.

Industrial Applicability

The electrochromic devices of the present invention exhibit optical transmission over large surface areas which is superior to that of previously known devices.

10

15

20

25

CLAIMS:

- An electrochromic device characterized by an electrochromic structure including an electrode (30) formed from an electrochromic material, counterelectrode (50) and transporting means (41) transporting ions between said electrode and said counterelectrode, conductive means including at least two electrically conductive layers (20, 22) sandwiching said electrochromic structure for applying an electric potential across said electrochromic structure, enhancing means (61) for enhancing the transmission of radiation through at least one of said electrically conductive layers, said electrochromic material having a first index of refraction, said counterelectrode having a second index of refraction and said transporting means having a third index of refraction, said first, second and third indices of refraction being about equal.
- 2. An electrochromic device as claimed in claim 1, wherein said electrochromic material is selected from the group consisting of tungsten oxide, niobium oxide, titanium oxide, molybdenum oxide, nickel oxide, iridium oxide, and mixtures thereof.
- 3. An electrochromic device as claimed in claim 1, wherein said counterelectrode is formed from a material selected from the group consisting of vanadium oxide, niobium oxide, indium oxide, nickel oxide, cobalt oxide, molybdenum oxide, and mixtures thereof.
- An electrochromic device as claimed claim 1, wherein said transporting means includes at 30 least one layer formed from an ion conducting material sandwiched between said electrode and said counterelectrode, said ion conducting material characterized by a lithium ion conducting lithium-based ceramic material.
- 5. An electrochromic device as claimed in claim 1, wherein said transporting means includes at least one layer formed from an ion conducting material sandwiched between said electrode and said

10

15

20

25

30

35

counterelectrode, said ion conducting material characterized by a hydrogen ion conducting material.

- 6. An electrochromic device as claimed in claim 1, wherein said transporting means includes at least one layer formed from an ion conducting material sandwiched between said electrode and said counterelectrode, said ion conducting material characterized by a polymer.
- 7. An electrochromic device as claimed in claim 1, wherein said enhancing means is characterized by at least one layer (61) of an optically transparent material for enhancing the transmission of radiation through said at least one electrically conductive layer and at least one other layer (62) of an optically transparent material for enhancing the transmission of radiation through another one of said electrically conductive layers.
- An electrochromic device characterized by an electrochromic structure including an electrode (30) electrochromic material, an formed counterelectrode (50) and transporting means (41) for transporting ions between said electrode and counterelectrode, conductive means including at least two electrically conductive layers (20, 22) sandwiching said electrochromic structure for applying an electric potential across said electrochromic structure, a base material (12), and enhancing means (61) including at least one layer of an optically transparent material arranged between said base material and at least one of said electrically conductive layers for enhancing the transmission of radiation through said at least one electrically conductive layer, said base material having a first index of refraction, said at least one electrically conductive layer having a second index of refraction, and said at least one layer of an optically transparent material having a third index of refraction between said first and second indices of refraction.

- 9. An electrochromic device as claimed in claim 8, wherein said third index of refraction is about equal to the square root of the mathematical product of said first and second indices of refraction.
- 10. An electrochromic device as claimed in claim 8, wherein said at least one layer of an optically transparent material has a thickness between about 60 nm and about 90 nm.
- 11. An electrochromic device as claimed in claim 8, wherein said at least one layer of an optically transparent material has a thickness which is inversely proportional to said third index of refraction.
 - 12. An electrochromic device as claimed in claim 8, wherein said enhancing means is further characterized by at least one other layer (62) of an optically transparent material for enhancing the transmission of radiation through another one of said electrically conductive layers.
- 13. An electrochromic device characterized by an electrochromic structure including an electrode (30) 20 from an electrochromic material. counterelectrode (50) and transporting means (41) transporting ions between said electrode and counterelectrode, conductive means including at least two electrically conductive layers (20, 22) sandwiching 25 said electrochromic structure for applying an electric potential across said electrochromic structure, a base material (12), and enhancing means for enhancing the transmission of radiation through at least one of said electrically conductive layers, said enhancing means 30 including a series of optically transparent beginning with a first optically transparent layer (64) arranged between said base material and said at least one electrically conductive layer and ending with an nth optically transparent layer (63) arranged between said 35 base material and said first optically transparent layer, said at least one electrically conductive layer having a first index of refraction, said base material

10

15

20

25

30

35

having a second index of refraction less than said first index of refraction, said first optically transparent layer having a third index of refraction less than said refraction, optically index of said nth first transparent layer having a fourth index of refraction greater than said second index of refraction, and said index of refraction of each one of said series of optically transparent layers decreasing monotonically from said third index of refraction to said fourth index of refraction.

14. An electrochromic device as claimed in claim 13, wherein said enhancing means is further characterized by at least one other layer (64) of an optically transparent material for enhancing the transmission of radiation through another one of said electrically conductive layers.

An electrochromic device characterized by an electrochromic structure including an electrode (30) electrochromic material, an from formed counterelectrode (50) and transporting means (41) for between said electrode and said ions transporting counterelectrode, conductive means including at least two electrically conductive layers (20, 22) sandwiching said electrochromic structure for applying an electric potential across said electrochromic structure, enhancing the transmission enhancing means for radiation through at least one of said electrically conductive layers, said enhancing means including two optically transparent layers (63, 64), one of said optically transparent layers being proximate to said at least one electrically conductive layer and another one of said optically transparent layers being distal to said at least one electrically conductive layer, said at least one electrically conductive layer having a first of said optically refraction, said one index of transparent layers having an index of refraction which is less than said first index of refraction, and said another one of said optically transparent layers having

15

an index of refraction which is greater than said index of refraction of said one of said optically transparent layers.

- 16. An electrochromic device as claimed in claim 15, wherein said one of said optically transparent layers has an index of refraction between about 1.4 and about 1.7, and said another of said optically transparent layers has an index of refraction about equal to or greater than said first index of refraction.
- 17. An electrochromic device as claimed in claim 15, wherein said two optically transparent layers have a combined thickness of between about 30 nm and about 70 nm.
 - 18. An electrochromic device as claimed in claim 15, wherein said enhancing means is further characterized by at least one other layer (64) of an optically transparent material for enhancing the transmission of radiation through another one of said electrically conductive layers.
- 20 An electrochromic device characterized by an electrochromic structure including an electrode (30) formed from an electrochromic material. counterelectrode (50) and transporting means (41) for transporting ions between said electrode and said counterelectrode, conductive means including at least 25 two electrically conductive layers (20, 22) sandwiching said electrochromic structure for applying an electric potential across said electrochromic structure, at least one of said electrically conductive layers including a 30 layer of an electrically conductive oxide, and enhancing means (61) for enhancing the transmission of radiation through said electrically conductive oxide layer, said electrochromic material having а first index refraction, said counterelectrode having a second index of refraction, said transporting means having a third 35 index of refraction, and said electrically conductive oxide layer having a fourth index of refraction, said

PCT/US93/12529

5

10

15

20

25

30

35

first, second, third and fourth indices of refraction being about equal.

- 20. An electrochromic device as claimed in claim 19, wherein said enhancing means is characterized by at least one layer (61) of an optically transparent material for enhancing the transmission of radiation through said electrically conductive oxide layer and at least one other layer (62) of an optically transparent material for enhancing the transmission of radiation through another one of said electrically conductive layers.
- An electrochromic device characterized by 21. an electrochromic structure including an electrode (30) electrochromic material. from an formed counterelectrode (50) and transporting means (41) for between said electrode and said transporting ions counterelectrode, conductive means including at least two electrically conductive layers (20, 22) sandwiching said electrochromic structure for applying an electric potential across said electrochromic structure, and means for enhancing the transmission enhancing radiation through said electrically conductive layers, said enhancing means including at least two optically layers (61, 62) sandwiching transparent electrochromic structure and said electrically conductive layers.
- 22. electrochromic combination characterized by a transparent substrate (12) and an electrochromic device arranged on said transparent device said electrochromic including substrate, electrochromic structure having an electrode (30) formed from an electrochromic material, a counterelectrode (50) transporting means (41) for transporting said counterelectrode, between said electrode and conductive means including at least two electrically 22) sandwiching conductive layers (20, said structure for applying electrochromic across said electrochromic structure, potential

10

15

20

25

30

enhancing means (61) for enhancing the transmission of radiation through at least one of said electrically conductive layers, said electrochromic material having a first index of refraction, said counterelectrode having a second index of refraction and said transporting means having a third index of refraction, said first, second and third indices of refraction being about equal.

- 23. An electrochromic combination as claimed 22, in claim wherein said enhancing means is characterized by at least one layer (61) of an optically transparent material arranged between said transparent substrate and said electrochromic device for enhancing the transmission of radiation through said at least one electrically conductive layer, and at least one other layer (62) of an optically transparent material for enhancing the transmission of radiation through another one of said electrically conductive layers.
- 24. An electrochromic combination as claimed in claim 22, further characterized by a transparent superstrate (14), wherein said electrochromic device is sandwiched between said transparent substrate and said transparent superstrate.
- 25. An electrochromic combination as claimed in claim 24. wherein said enhancing means is characterized by at least one layer (61) of an optically transparent material arranged between said transparent substrate and said electrochromic device for enhancing the transmission of radiation through said at least one electrically conductive layer, and at least one other layer (62) of an optically transparent material arranged said transparent superstrate electrochromic device for enhancing the transmission of radiation through another one of said electrically conductive layers.
- 26. An electrochromic combination as claimed in claim 24, further characterized by a layer of an adhesive material (70) for binding said transparent superstrate to said electrochromic device.

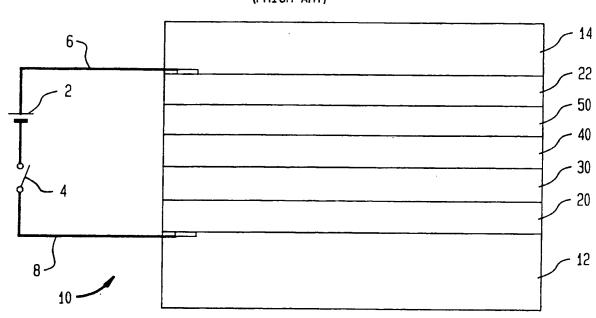
- 27. An electrochromic combination as claimed in claim 26, wherein said adhesive layer has an index of refraction between about 1.4 and about 1.8.
- in claim 26, wherein said transparent superstrate has an index of refraction and said adhesive layer has an index of refraction which is substantially equal to said index of refraction of said transparent superstrate.
- 29. An electrochromic combination as claimed in claim 26, wherein another of said electrically conductive layers includes a layer of an electrically conductive oxide and said adhesive layer is in surface contact with said electrically conductive oxide layer.
- in claim 29, wherein said electrically conductive exide layer has one index of refraction, said transparent superstrate has another index of refraction, and said adhesive layer has an index of refraction between said one and said another indices of refraction.

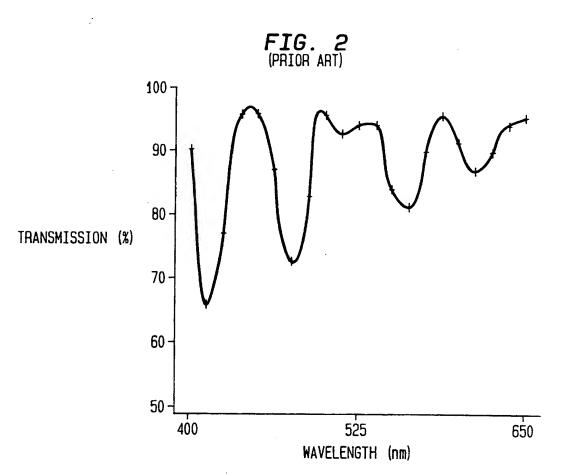
20

25

30

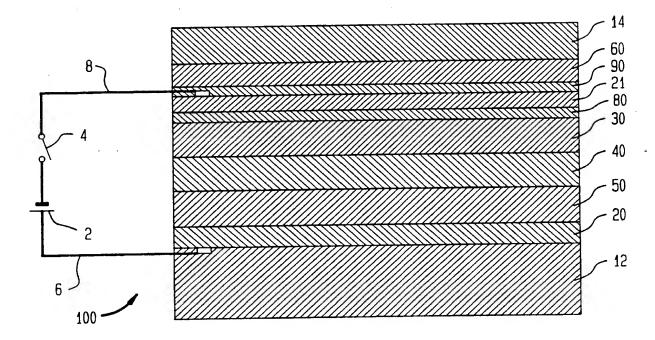
FIG. 1 (PRIOR ART)

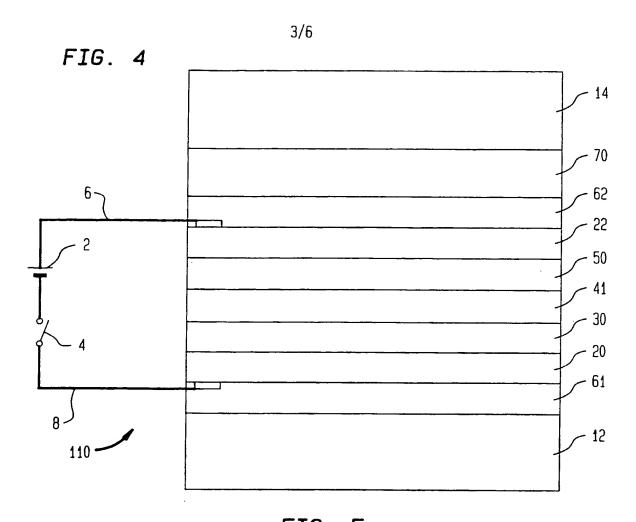


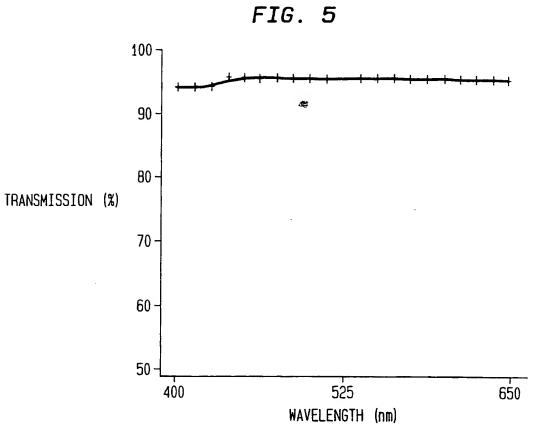


2/6

FIG. 3







PCT/US93/12529

- 12

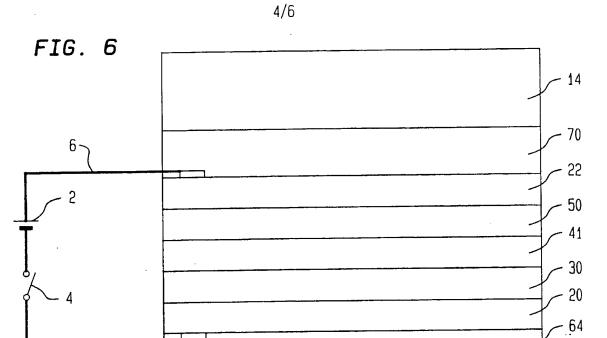
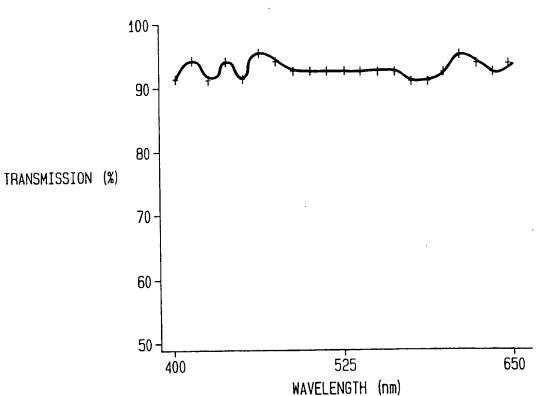
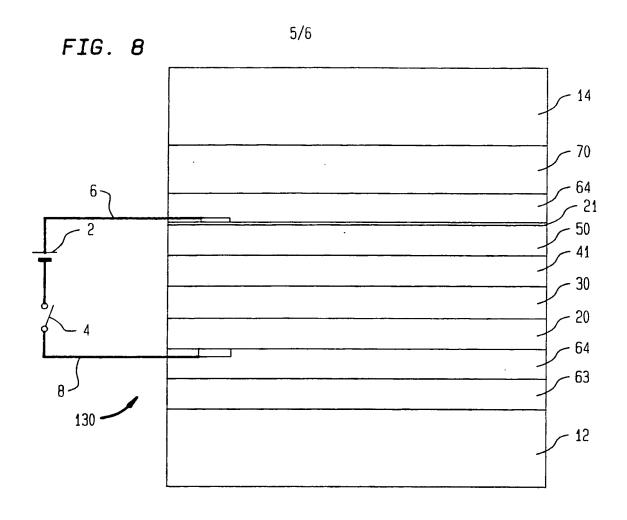
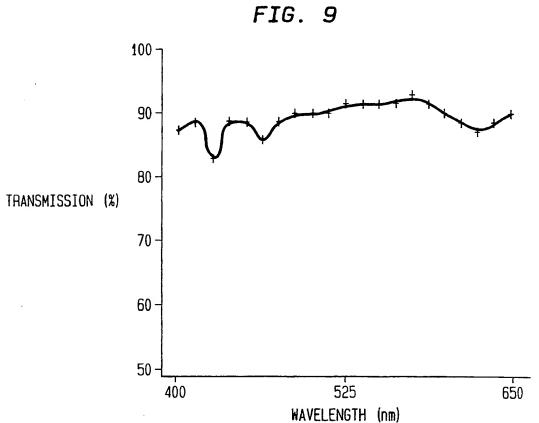
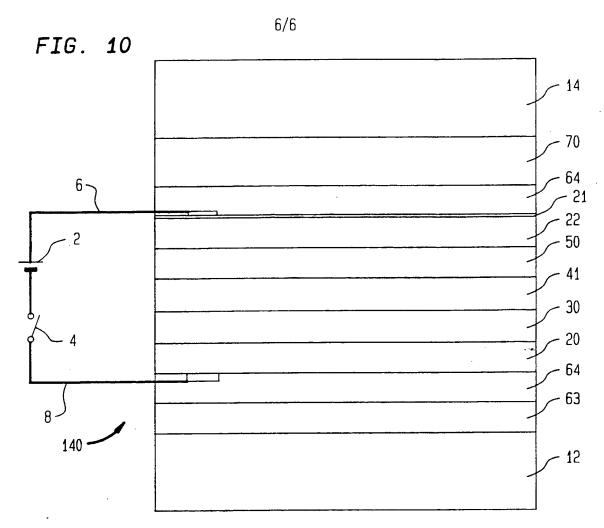


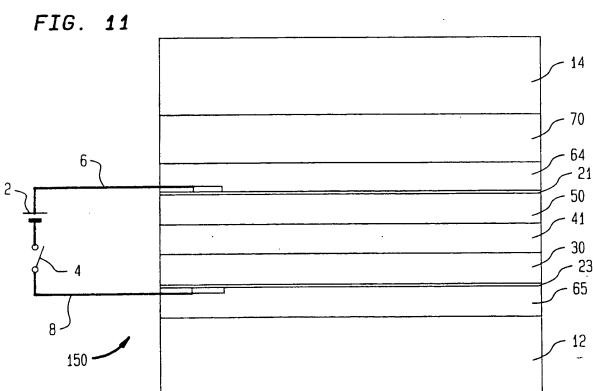
FIG. 7











A. CLASSIFICATION OF SUBJECT MATTER IPC(5):G02F 1/153, 1/155 US CL:359/265,266,273,274,275 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S.: 359/265,266,273,274,275 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched								
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)								
C. DOCUMENTS CONSIDERED TO BE RELEVANT								
Category* Citation of document, with indication, where a	ppropriate, of the relevant passages	Relevant to claim No.						
X Y US, A, 5,130,842 (GAUTHIER et figure 2 and the detailed description A US, A, 5,007,718 (MINOURA et al.) WO, 89/12,844 (COGAN et al.) WO, 89/09428 (IIHAGE) 5 October	on. al) 16 April 1991 8 December 1989	21 1-8,10,12, 19,20, 22-29 1-30 1-30						
Further documents are listed in the continuation of Box C Special categories of cited documents: A* document defining the general state of the art which is not considered to be part of particular relevance E* earlier document published on or after the international filing date L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) O* document referring to an oral disclosure, use, exhibition or other means P* document published prior to the international filing date but later than the priority date claimed Date of the actual completion of the international search O7 February 1994 Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	See patent family annex. The later document published after the interest and not in conflict with the applic principle or theory underlying the interest of the considered novel or cannot be considered novel or cannot be considered novel or cannot be considered to involve an inventive combined with one or more other successing obvious to a person skilled in the document member of the same patent of mailing of the international search of the same patent of the same	ation but cited to understand the vention se claimed invention cannot be cred to involve an inventive step se claimed invention cannot be step when the document is a documents, such combination he art I family arch report						

Form PCT/ISA/210 (second sheet)(July 1992)*